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To cite this article: Xingrong Zheng 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **295** 032041

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# Many-body effects on Equation of state of solid Ar<sub>4</sub>

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**Abstract.** Based on the first-principles, using many-body expansion method and the double cluster with full single and double excitations plus perturbative treatment of triples (CCSD(T)) calculation method and augmented correlation consistent quadruple zeta (aug-cc-pVQZ) basis set, many-body contributions to the equation of state (EOS) of solid argon are accurately calculated with the atomic distance  $R$  from 2.0Å to 3.6Å at the room temperature ( $T=300\text{K}$ ) in the experimentally studied range of pressures (0~80GPa). In addition, we obtain the two- and three-body potential energies of fcc solid Ar. The results showed that, only taking into account the two-body potential, our calculated results were in good agreement with the experimental values, the results of GGA and LDA at the low-pressure regions (<15GPa). Further adding three-body term up to 80GPa, and it may be helpful to accurately explain the phenomenon of the experiment above 80GPa when the effect of four-body and higher-body potential pressures are considered.

## 1. Introduction

As one of the two classification of solid materials, crystal has important research value in material fields. Some crystal displays obvious symmetry and periodicity in the geometry, such as hexagonal and cubic symmetry, and these symmetry not only reflect the geometry shape, but also manifest the macroscopic physical properties of lattice, such as volume, pressure, etc., which it is extremely significant[1-3]. Solid argon (Ar) is most acquired in rare gases, and many properties have been researched in the condensed matter physics and materials [4-9], including theory and experiment. In addition, Ar can be used as pressure medium in the high-pressure experiments [8,9]. And the X-ray diffraction measurements of solid Ar has been compressed to 114GPa at room temperature [10], the volume compression ratio is 3.06. Therefore, it attracts much theoretical research interests for solid Ar. In the current studies, the many-body interaction potential energy is most interesting for the researchers. The two-body and three-body potential energies and equation of state of solid Ar have reported in the interaction potential aspects [11-17], including the theoretical and experimental studies, while the other aspects of two- and three-body potentials less are discussed. The two-body potential includes the Hartree-Fock potential and the correlation potential, and the three-body potential contains the self-consistent-field Hartree-Fock and the correlation parts.

In this work, using CCSD(T) calculation method and aug-cc-pVQZ basis set, we accurately calculate two- and three-body potential energies of face-centered cubic (fcc) solid Ar with the atomic distance  $R$  from 2.0Å to 3.6Å at  $T=300\text{K}$ . Then, we obtain the equation of state (EOS) of solid Ar which can accurately described the compression characteristics of many-body potential in the experimentally studied range of pressures (0~80GPa), and hope to accurately explain the phenomenon of the experiment above 80GPa when higher many-body potential are considered.



## 2. Theoretical derivations

The experiments shows that solid  $Ar$  is a face-centered cubic crystal structure (fcc) in ordinary environment. Based on the symmetry and periodicity of crystal, the cohesive energy ( $E(V)$ ) of fcc solid  $Ar$  is a function of volume ( $V$ ), which can be expanded to a series of many-body potentials, such as two-, three-body term [18].

$$\begin{aligned} E(V) &= E_2(V) + E_3(V) + \dots \\ &= \frac{1}{2}U_2(o) + \frac{1}{3}U_3(o) + \dots \\ &= \frac{1}{2} \sum_{i=1}^{n-1} u_2(o, i) + \frac{1}{3} \sum_{1=i < j}^{n-1} u_3(o, i, j) + \dots \end{aligned} \quad (1)$$

Where  $E_n(V)$  represents the  $n$ -body cohesive energy.  $U_2(o)$  is two-body total potential energy between the central atom  $o$  and its neighbours, and  $U_3(o)$  is three-body total potential energy. While two- and three-body potentials are expressed by

$$u_2(o, i) = E(r_o, r_i) - 2E_0, \quad (2)$$

$$u_3(o, i, j) = E(r_o, r_i, r_j) - 3E_0 - \sum_{i=1}^{n-1} u_2(o, i), \quad (3)$$

where  $E_0$  represents the ground state energy of the isolated atom,  $i$  and  $j$  denotes different neighbours of the central atom  $o$ ,  $(n-1)$  denotes the total number of considered neighbours. These terms are calculated at CCSD(T) calculation method by Gamess software [19].

The pressure is a function of volume ( $V$ ) and temperature ( $T$ ) which consist of the many-body static pressures, zero-point vibrational pressure and thermal pressure.

$$P(V, T) = P_2(V) + P_3(V) + P_{zp}(V) + P_{th}(V, T), \quad (4)$$

where the many-body pressure term  $P_n$  can be expressed by

$$P_n(V) = -\frac{\partial E_n(V)}{\partial V}, \quad (n = 2, 3). \quad (5)$$

Using the Mie-Grüneisen-Debye approach [20], the zero-point vibrational pressure  $P_{zp}$  and the thermal pressure  $P_{th}$  can be written as

$$P_{zp}(V) = \frac{\gamma}{V} E_{zp}, \quad (6)$$

$$P_{th}(V, T) = \frac{\gamma 9 k_B T}{V} \left(\frac{\Theta}{T}\right)^{-3} \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx, \quad (7)$$

where  $k_B$  is the Boltzmann constant,  $\Theta$  is the Debye temperature, and  $\gamma$  is the Grüneisen coefficient, the zero-point vibrational energy  $E_{zp}$  can be expressed by

$$E_{zp} = \frac{9}{8} k_B \Theta. \quad (8)$$

## 3. The calculation results and discussion

### 3.1 Two- and three-body cohesive energies

Using CCSD (T) calculation method, we calculate the two- and three-body potential energies of fcc solid  $Ar$  at  $R=2.0\sim 3.6\text{\AA}$ , then obtain the two- and three-body cohesive energies by FORTRAN77 Programme, as listed in Table 1. The last column is the ratio between the three-body cohesive energy and the two-body cohesive energy, reflecting the role of three-body term in many-body cohesive energy. The results show that the even many-body contributions to the cohesive energy, such as the

two-body, the four-body contributions to the cohesive energy, are repulsive. Whereas, the odd many-body contributions to the cohesive energy, such as the three-body potential, the five-body potential, are attractive. In addition, we also find that three-body cohesive energy of solid *Ar* is very slight compared with that of two-body cohesive energy when the atomic distance  $R$  higher than  $3.0\text{\AA}$ . When  $R > 3.0\text{\AA}$ ,  $-E_3/E_2 < 5\%$ , which means the role of three-body term is small. With the decrease of the atomic distance  $R$ , the ratio between the three-body cohesive energy and the two-body cohesive energy increase. For example, the atomic distance  $R = 2.8\text{\AA}$ ,  $-E_3/E_2 > 10\%$ , so the three-body potential is not been ignored. When  $R = 2.0\text{\AA}$ , the ratio up to  $54.1\%$ . Therefore, when the atomic distance  $R$  lower than  $2.0\text{\AA}$ , the ratio between them will become large, and the compressibility for solid *Ar* will become bigger. It is concluded that the two-body term can not accurately describe the properties of cohesive for solid *Ar* when  $R$  reduces to a constant value, so it need to consider the three-body, four-body and higher-body potential for solid *Ar*.

TABLE 1 The two-body and three-body cohesive energies of solid fcc *Ar*. where  $E_{23} = E_2 + E_3$ .

$R$ ( $\text{\AA}$ )	$V$ ( $\text{cm}^3/\text{mol}$ )	$E_2$ (K)	$E_3$ (K)	$E_{23}$ (K)	$\frac{E_2}{E_{23}}$	$\frac{E_3}{E_{23}}$	$-\frac{E_3}{E_2}$
2.0	3.407	323247.8	-174934.5	148313.3	2.1795	-1.17949	0.54118
2.1	3.944	227911.1	-100041.9	127869.2	1.7824	-0.78238	0.43895
2.2	4.534	159430.1	-57088	102342.1	1.5578	-0.55782	0.35808
2.3	5.181	110566.2	-32423	78143.2	1.4149	-0.41492	0.29325
2.4	5.887	75928.5	-18277.6	57650.9	1.3170	-0.31704	0.24072
2.5	6.653	51537.7	-10192.2	41345.5	1.2465	-0.24651	0.19776
2.6	7.484	34481.9	-5593	28888.9	1.1936	-0.1936	0.1622
2.7	8.381	22646.7	-2993.6	19653.1	1.1523	-0.15232	0.13219
2.8	9.348	14506.7	-1538.9	12967.8	1.1187	-0.11867	0.10608
2.9	10.385	8967	-737.7	8229.3	1.0896	-0.08964	0.08227
3.0	11.497	5245	-308.4	4936.6	1.0625	-0.06247	0.0588
3.1	12.686	2784.3	-88.5	2695.8	1.0328	-0.03283	0.03179
3.2	13.953	1191.1	15.3	1206.4	0.9873	0.01268	-0.01285
3.3	15.303	188.6	56.9	245.5	0.7682	0.23177	-0.3017
3.5	18.257	-758.9	63.2	-695.7	1.0908	-0.09084	0.08328
3.6	19.867	-929.8	54.4	-875.4	1.0621	-0.06214	0.05851

Using CCSD (T) method, it not only obtain the curves of the two-body and three-body cohesive energies with data of TABLE 1, but also make a comparison between theoretical computed results of this work and the former theoretical results [11,14-16], as seen in Figure 1. For the two-body cohesive energy, this calculated result and the former calculated results [11,14,15] have a good agreement at  $R > 2.3\text{\AA}$ , but there is a difference among the four curves at the smaller value of  $R$ . For the three-body cohesive energy, our results is consistent with the former results[16]. It is concluded that the three-body contribution to the cohesive energy is considered, the two curves of the total cohesive energy  $E_{23}$  of our calculated results and Freiman's results [16] are almost coincident at studied range of  $R = 2.0 \sim 3.6\text{\AA}$ . The conclusion shows that the calculation method of this work is precise and feasible. In addition, the zero-point vibrational energy  $E_{zp}$  of fcc solid *Ar* is calculated by Deybe approximation, as shown in Fig.1. The results show that the zero-point vibration energy is very small which is about 5% of the many-body interaction energy, so it should not be neglected, and the molar volume of the crystal is smaller, the zero-point vibration energy is greater.

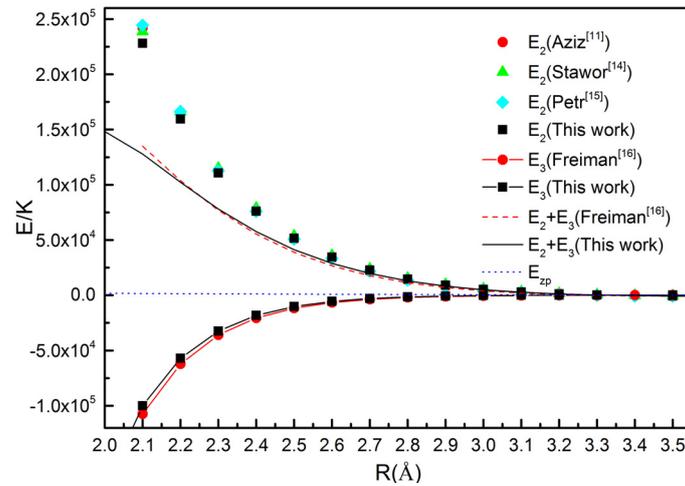


Figure 1 Comparison of the two-body, three-body cohesive energies in fcc *Ar* with the previous results. The dashed line represents the zero-point vibrational energy of fcc solid *Ar*.

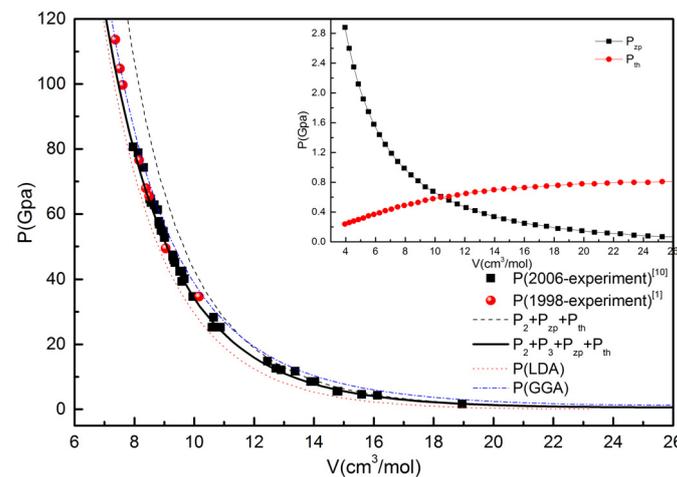


Figure 2 Comparison between the theoretical and experimental equations of state for solid *Ar*. The inset shows the zero-point vibrational pressure  $P_{zp}$  and the thermal pressure  $P_{th}$  are a function of molar volume  $V$ .

### 3.2 Equation of state

Using Eq. (4), we obtain the equations of state of fcc solid *Ar* at  $T=300\text{K}$ , and the calculated  $T=300\text{K}$  dependence of  $P(V)$  for solid *Ar* is seen in Figure 2 along with the experimental results [1,10].  $P_n(V)$  ( $n=2, 3$ ) are static pressure term which are caused by many-body interactions,  $P_{zp}$  is zero-point vibration pressure which is caused by zero-point vibration,  $P_{th}$  is the thermal pressure which is caused by temperature. The inset in the upper-right corner shows the zero-point vibrational pressure  $P_{zp}$  and the thermal pressure  $P_{th}$  are a function of molar volume  $V$ . We find that the zero-point vibration energy  $P_{zp}$  and the thermal pressure  $P_{th}$  of solid *Ar* are very small which only are less than 5% of the total pressures, but shall not be neglected. Finally, we also calculate the equation of state for fcc *Ar* with the generalized gradient approximation (GGA) and the local-density approximation (LDA) based on density functional theory, and compare with our calculated results. It are seen that only taking into account the two-body potential pressure  $P_2 + P_{zp} + P_{th}$ , our calculated results and the experimental results are in good agreement with the experimental values, the results of GGA and LDA at the low-pressure regions ( $<10\text{GPa}$ ). Considering the two- and three-body potential pressure  $P_2 + P_3 + P_{zp} + P_{th}$ , they have a good consistency at pressure range 10-80GPa. At higher pressure zones ( $>80\text{GPa}$ ), our

calculated results and the experimental values, the results of GGA and LDA have deviation, in which it need consider the effect of four-body, five-body potential pressure. Here, only considering two- and three-body potential pressure  $P_2+P_3$ , the isothermal compression properties for solid Ar between our results and the experimental results, the results of GGA and LDA have a good consistency at the current experimental ranges 0~80GPa, and we expect that the phenomenon of the experiment above 80GPa may be explained accurately when the effect of higher-body potential pressures are considered.

#### 4. Conclusions

Based on the first-principles, combined face-centered cubic (fcc) atomic crystal configuration, using the many-body expansion method and the double cluster with full single and double excitations plus perturbative treatment of triples calculation method and augmented correlation consistent quadruple zeta basis set, we accurately calculate two- and three-body cohesive energy and equation of state (EOS) of solid argon with the atomic distance  $R$  from 2.0Å to 3.6Å at the room temperature ( $T=300\text{K}$ ) in the experimentally studied range of pressures (0~80GPa). Then we obtain the two- and three-body potential energies of fcc solid Ar, we find that the even many-body contributions to the cohesive energy, such as the two-body, the four-body contributions to the cohesive energy, are repulsive. Whereas, the odd many-body contributions to the cohesive energy, such as the three-body potential, the five-body potential, are attractive. Furthermore, we also calculate the equation of state for fcc Ar with the generalized gradient approximation (GGA) and the local-density approximation (LDA) based on the density functional theory, and compare with our calculation results. Only taking into account the two-body potential, our calculated results are in good agreement with the GGA, LDA results and the experimental values at the low-pressure regions (<15GPa). Further adding three-body term up to 80 Gpa, and may be helpful to accurately explain the phenomenon of the experiment above 80Gpa when the effect of four-body, higher-body potential pressures are considered.

#### Acknowledgement

The research were sponsored by National Natural Science Foundation of China (NSFC) (11565018) and Gansu province Department of Education fund item (2019A-101).

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